An Initial Look at Testing Photochemical Theory During INTEX

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Purpose:

Characterize the relationship between measurements and photochemical theory

Ultimate Goals:

Seek to understand differences between observations and expectations based on current knowledge

Estimate the contribution of photochemistry to the observed ozone distribution

Assess the impact of convection on chemical processing in the upper troposphere

Assess the impact of NMHCs on ozone and oxidant levels

Time-dependent photochemical box model

Detailed HO_x-NO_x-CH_4-NMHC mechanism

Constrained by observations:
T, P, H_2O, O_3, CO, NO, non-methane hydrocarbons, acetone, photolysis rates

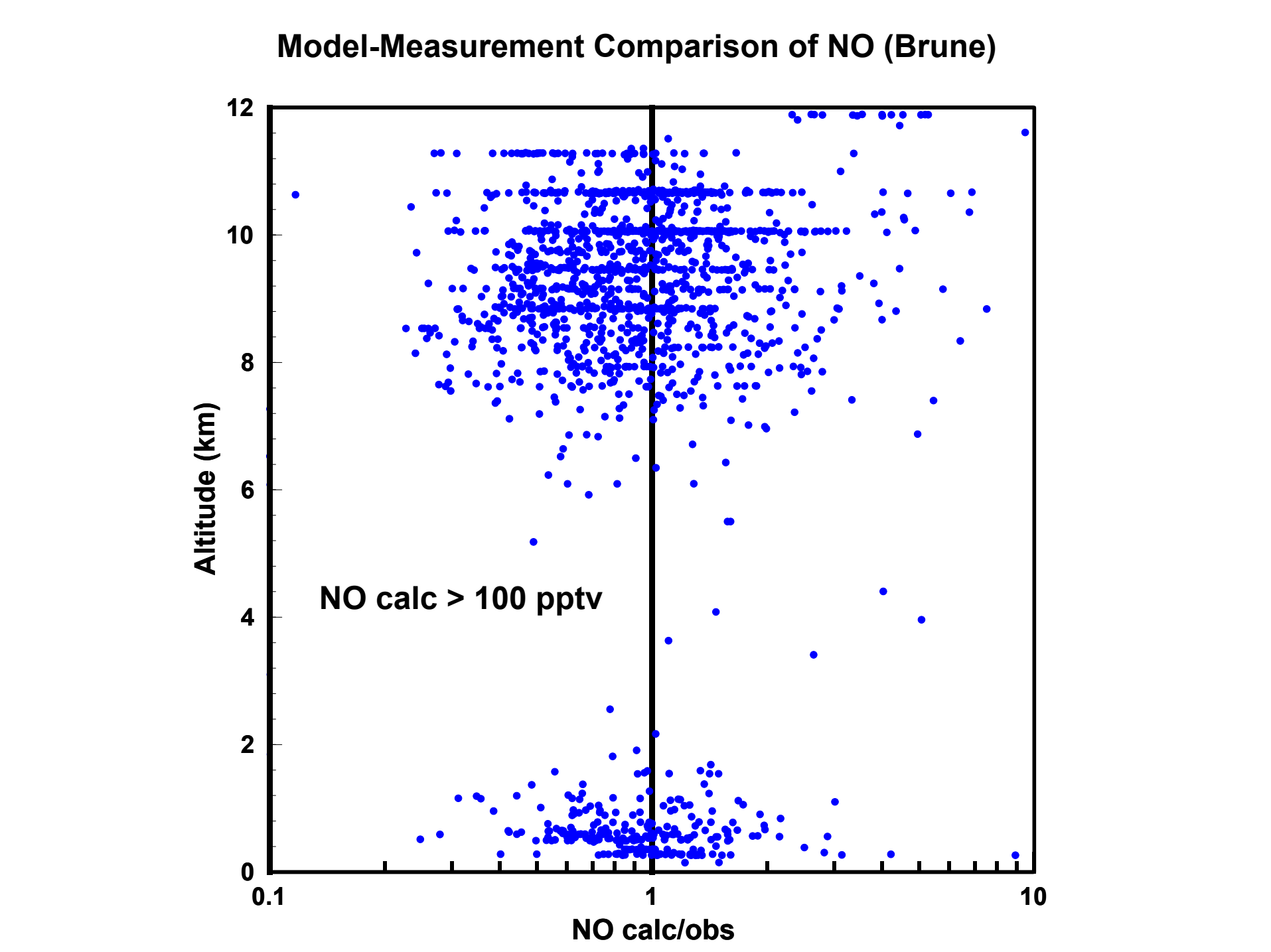
When observations are available, additional model constraints include:
H_2O_2, CH_3OOH, HNO_3, PAN, HCOOH, CH_3COOH

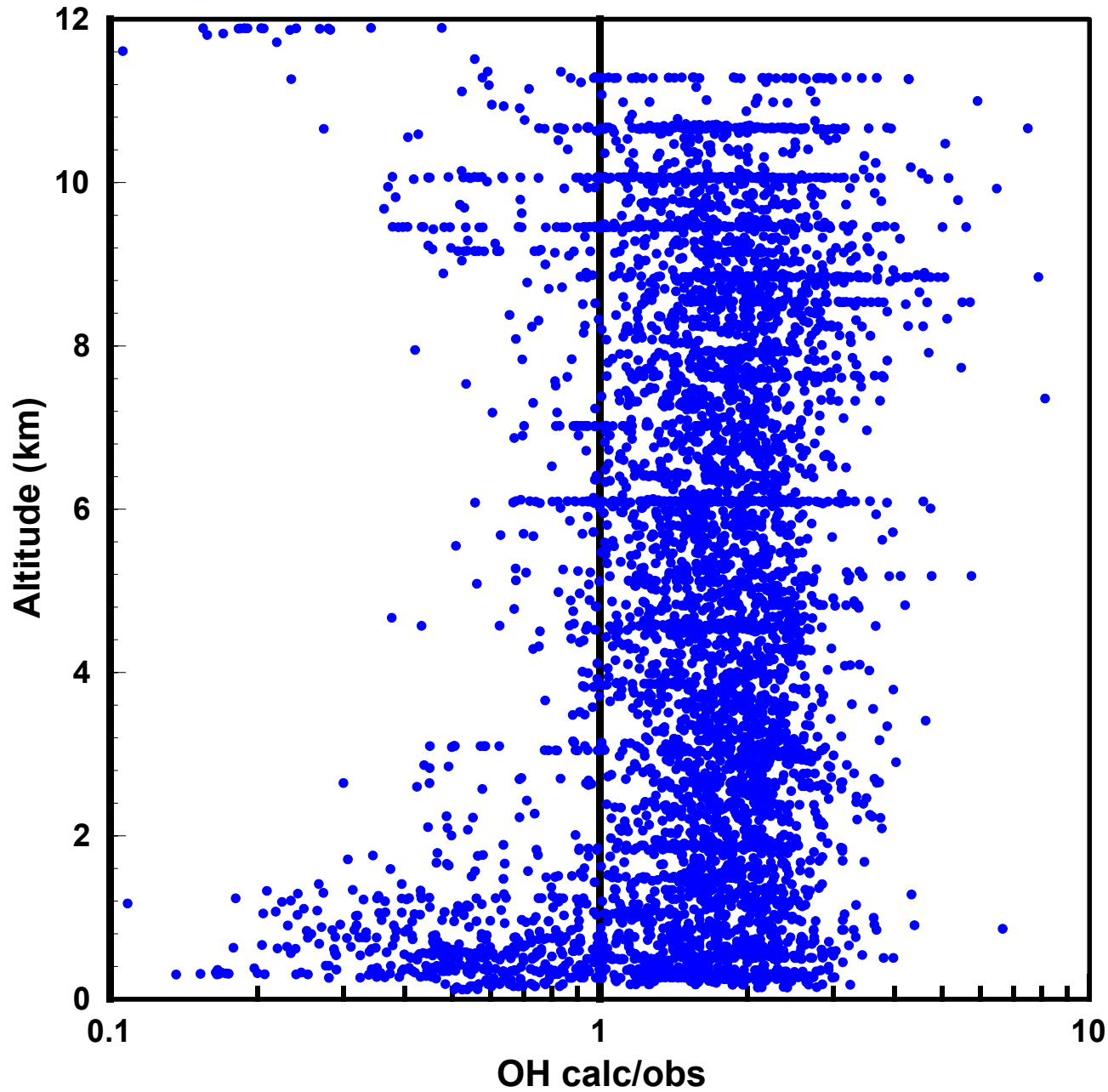
Predicted species:
OH, HO_2, RO_2, CH_2O, H_2O_2, CH_3OOH, ROOH, NO_2, HNO_3, PAN, ROOH, etc.

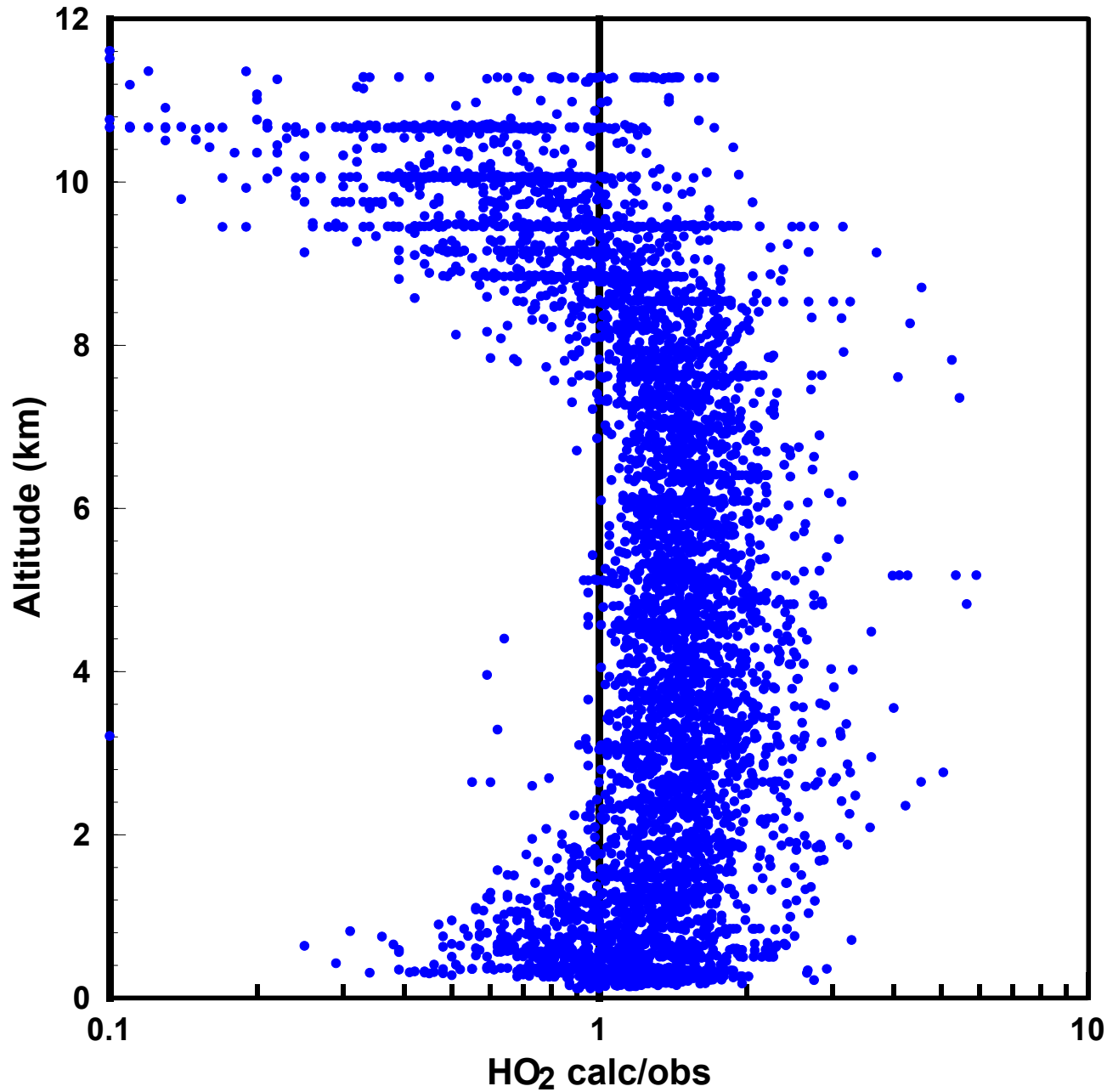
Calculated species are integrated in time until diurnal profile converges.

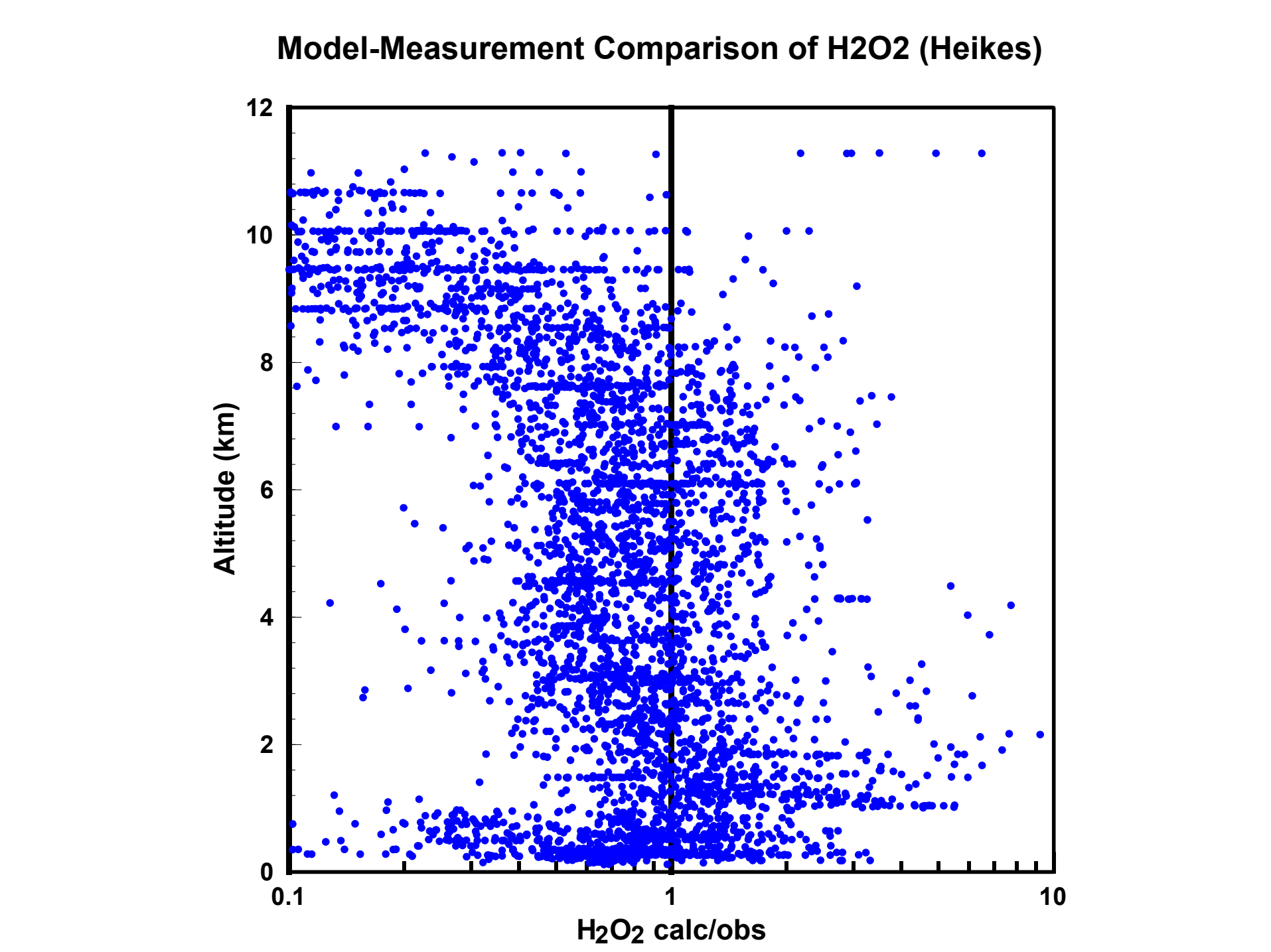
NO_x held constant, but partitioning varies throughout the diurnal cycle

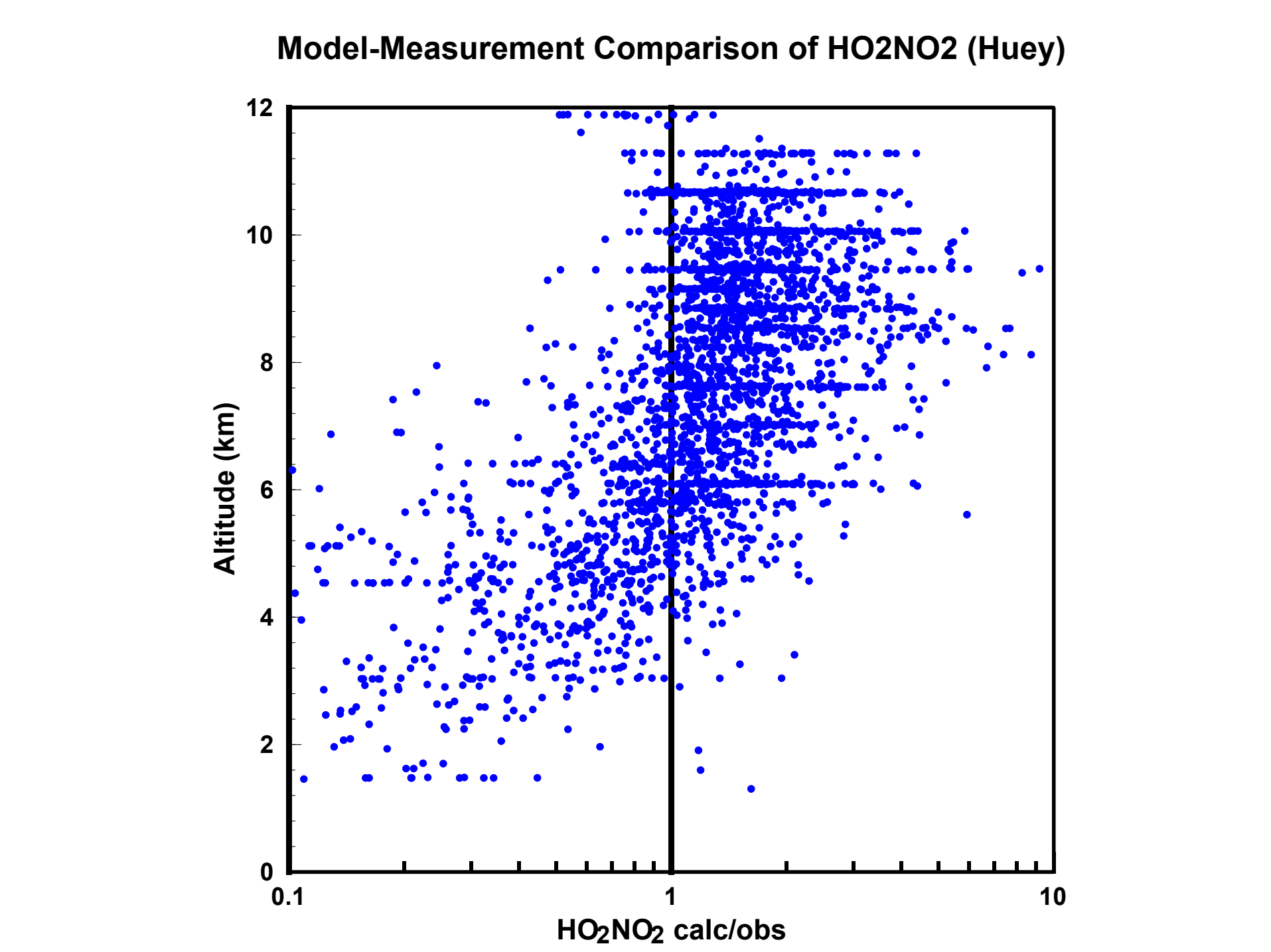
Diurnal variation of photolysis rates from TUV (DISORT 8 streams)

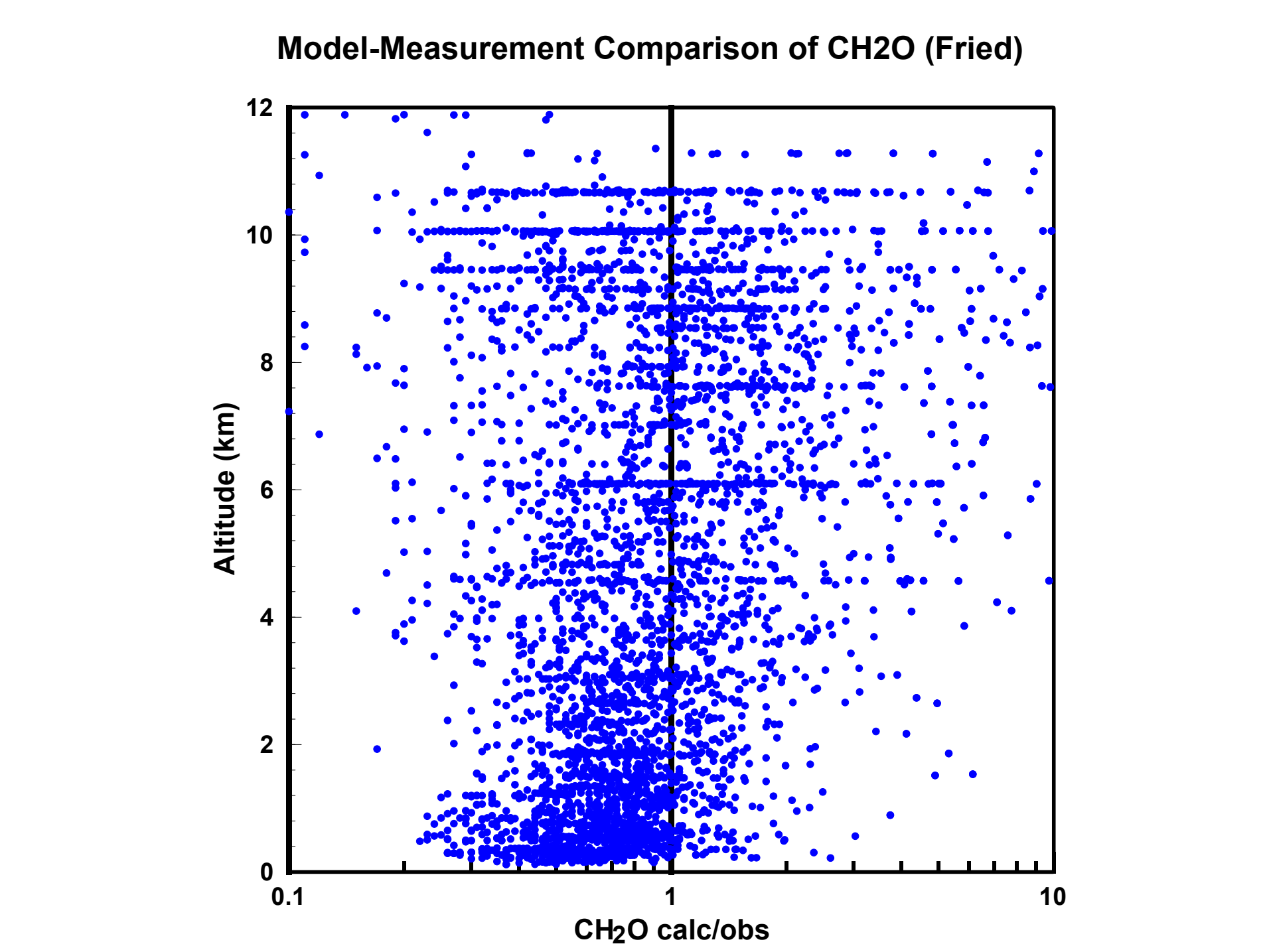

Model-Measurement Comparison of NO (Brune)
Altitude (km)
12
10
8
6
4
2
0
0.1
1
10
NO calc/obs
NO calc > 100 pptv

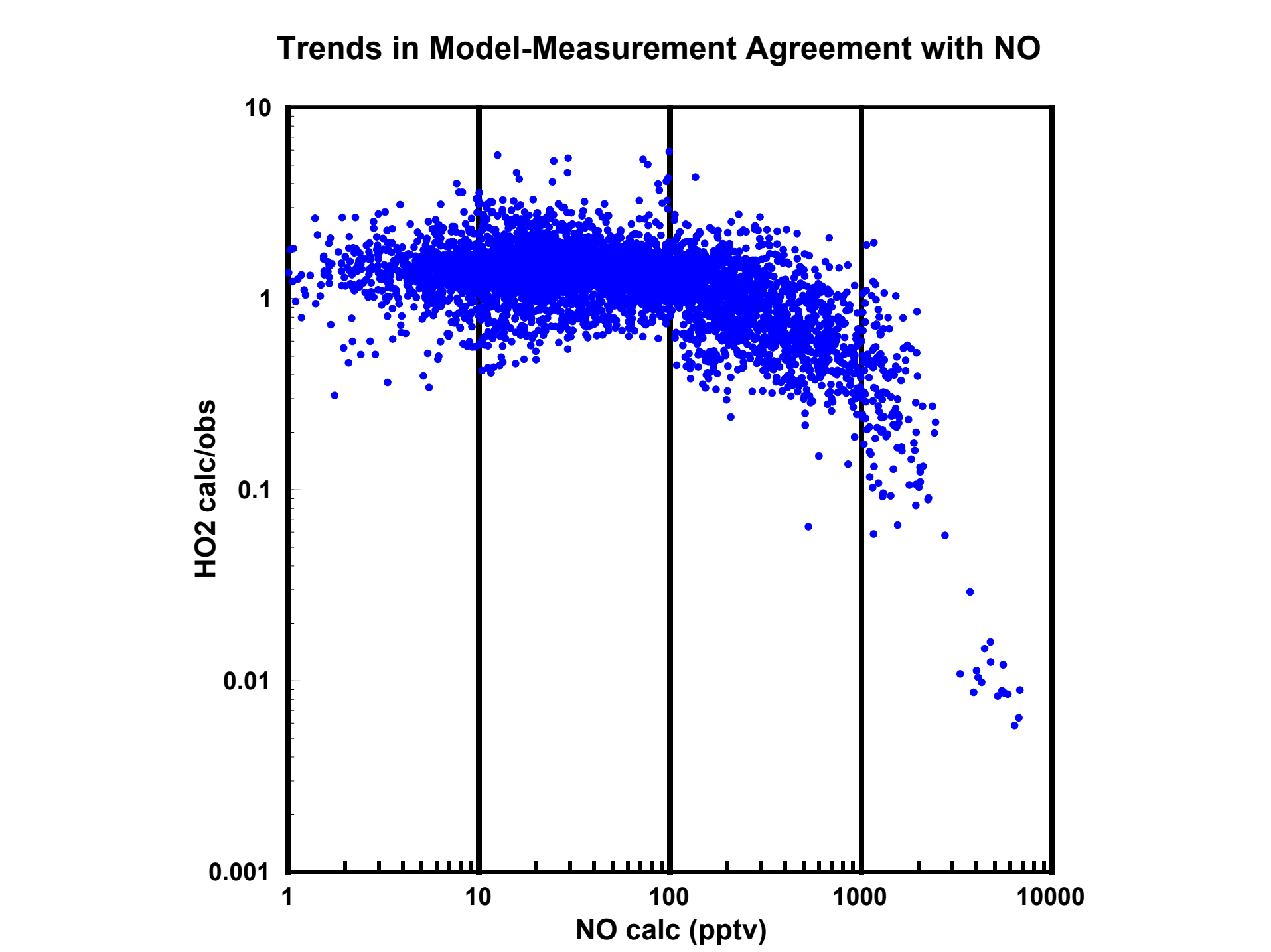

Model-Measurement Comparison of OH (Brune)
Altitude (km)
0
2
4
6
8
10
12
0.1
1
10
OH calc/obs

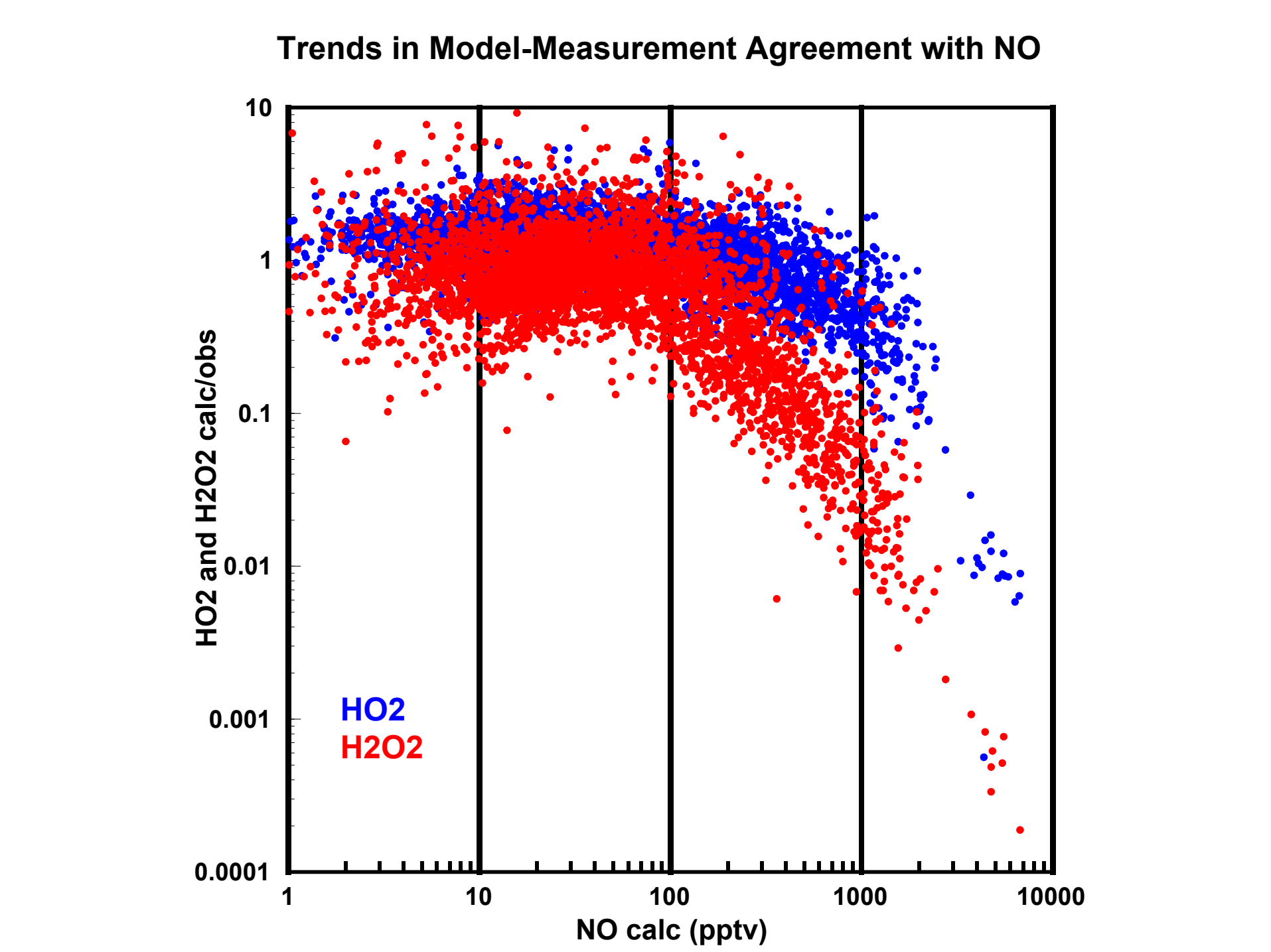

Model-Measurement Comparison of HO2 (Brune)
Altitude (km)
0
2
4
6
8
10
12
0.1
1
10
HO2 calc/obs

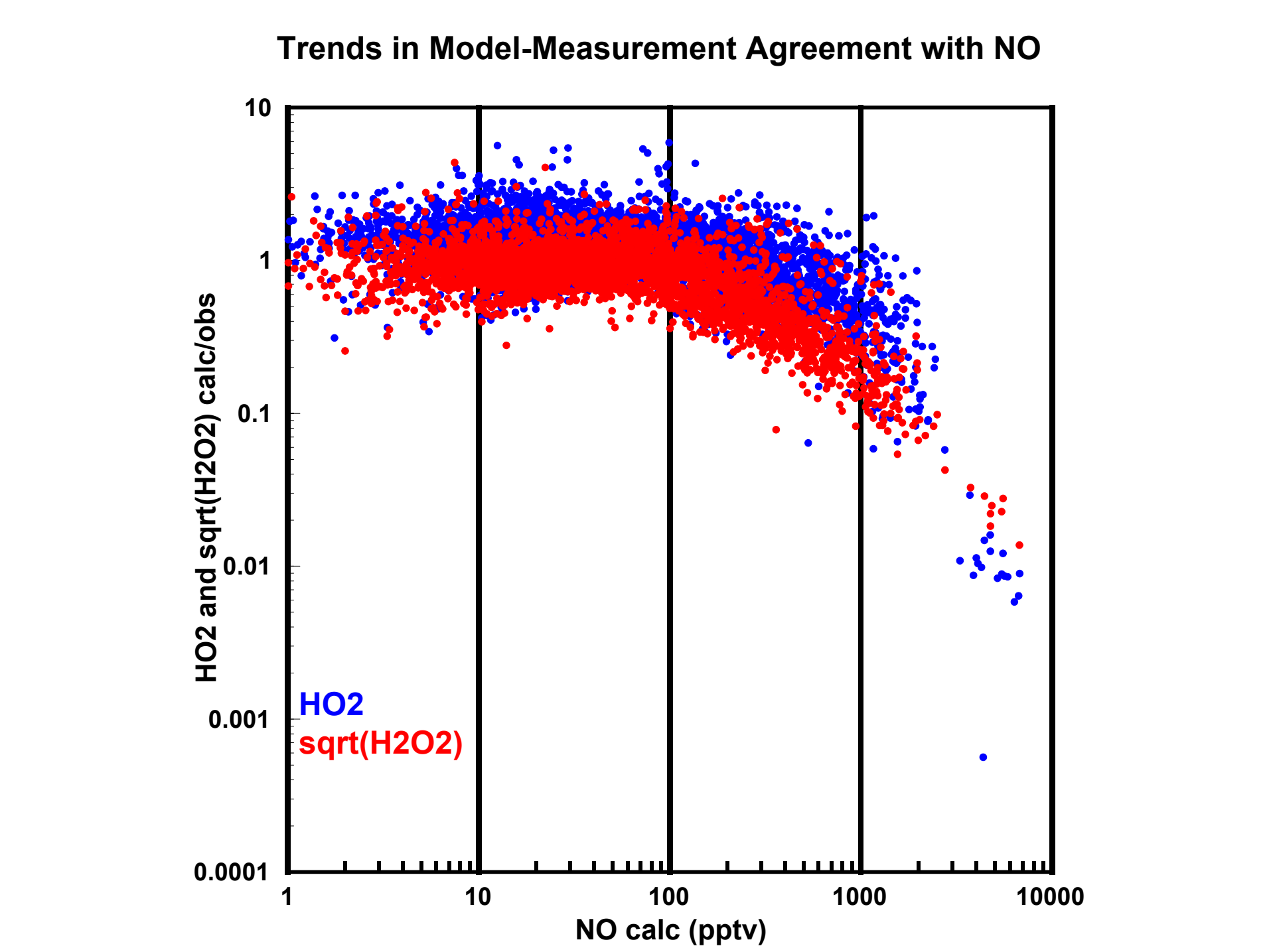

Model-Measurement Comparison of H2O2 (Heikes)
Altitude (km)
0
2
4
6
8
10
12
0.1
1
10
H2O2 calc/obs

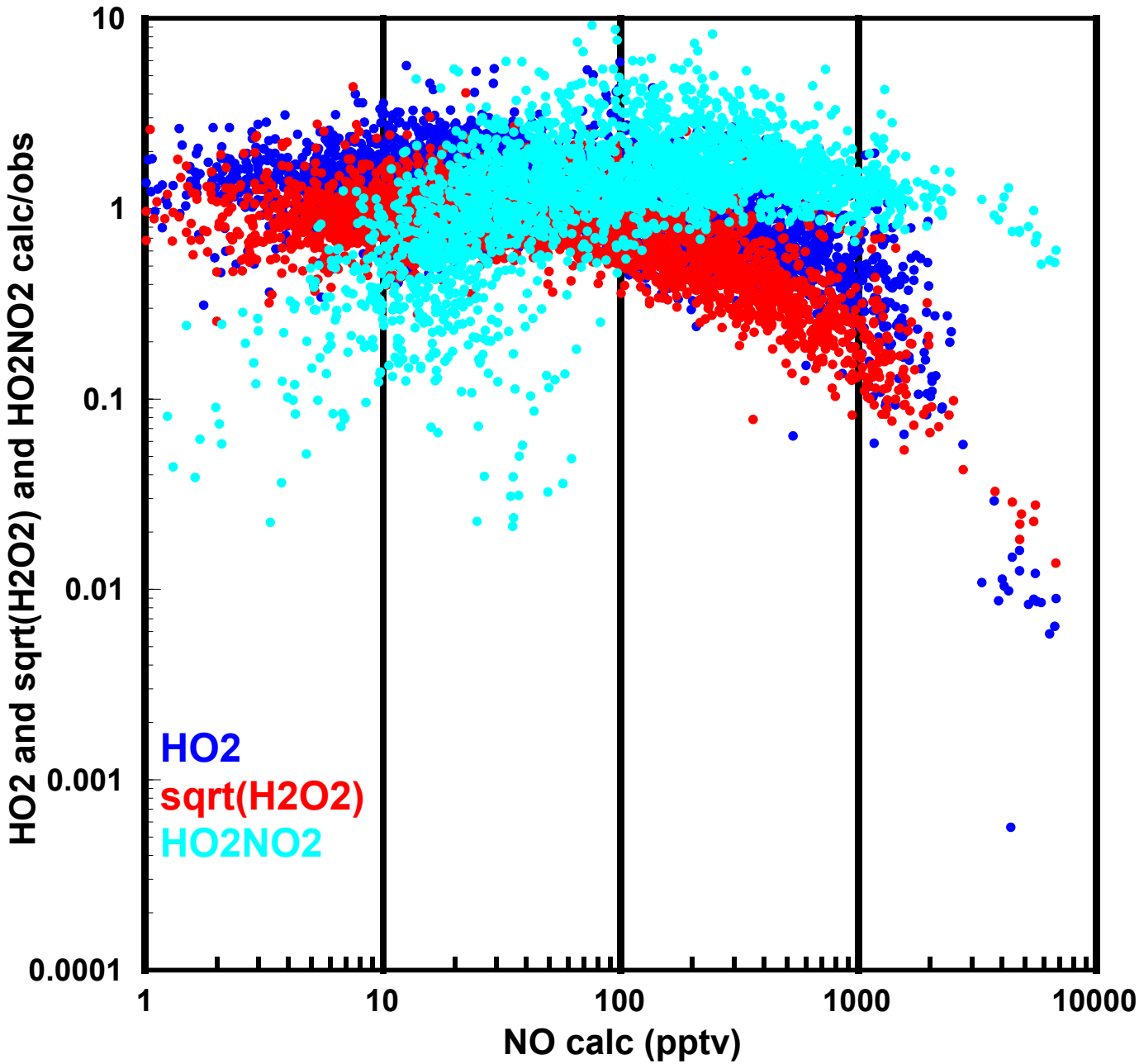

Model-Measurement Comparison of HO2NO2 (Huey)
Altitude (km)
0
2
4
6
8
10
12
0.1
1
10
HO2NO2 calc/obs


Model-Measurement Comparison of CH2O (Fried)
Altitude (km)
0
2
4
6
8
10
12
0.1
1
10
CH2O calc/obs

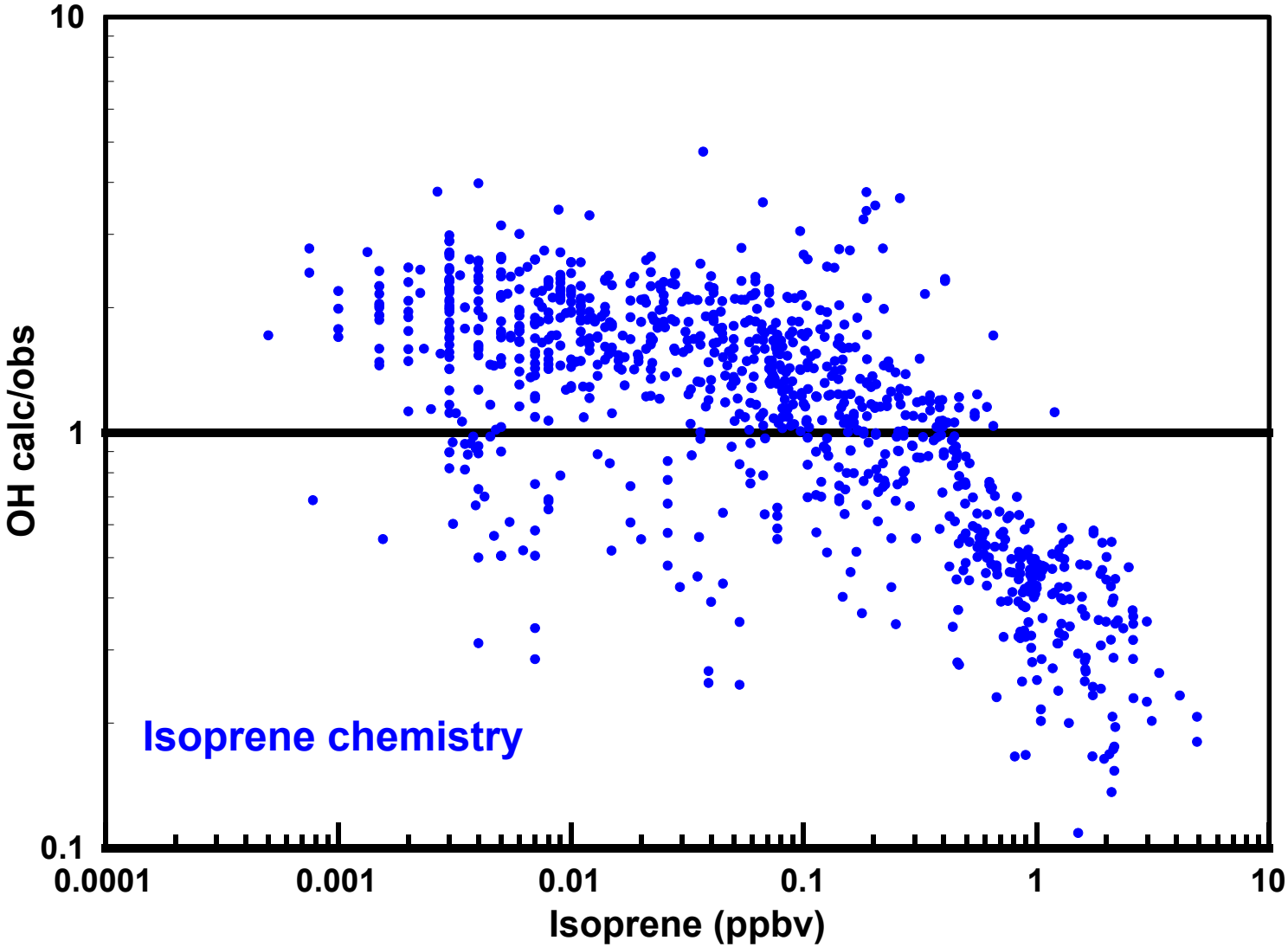

Trends in Model-Measurement Agreement with NO
HO2 calc/obs
10
1
0.1
0.01
0.001
1
10
100
1000
10000
NO calc (pptv)

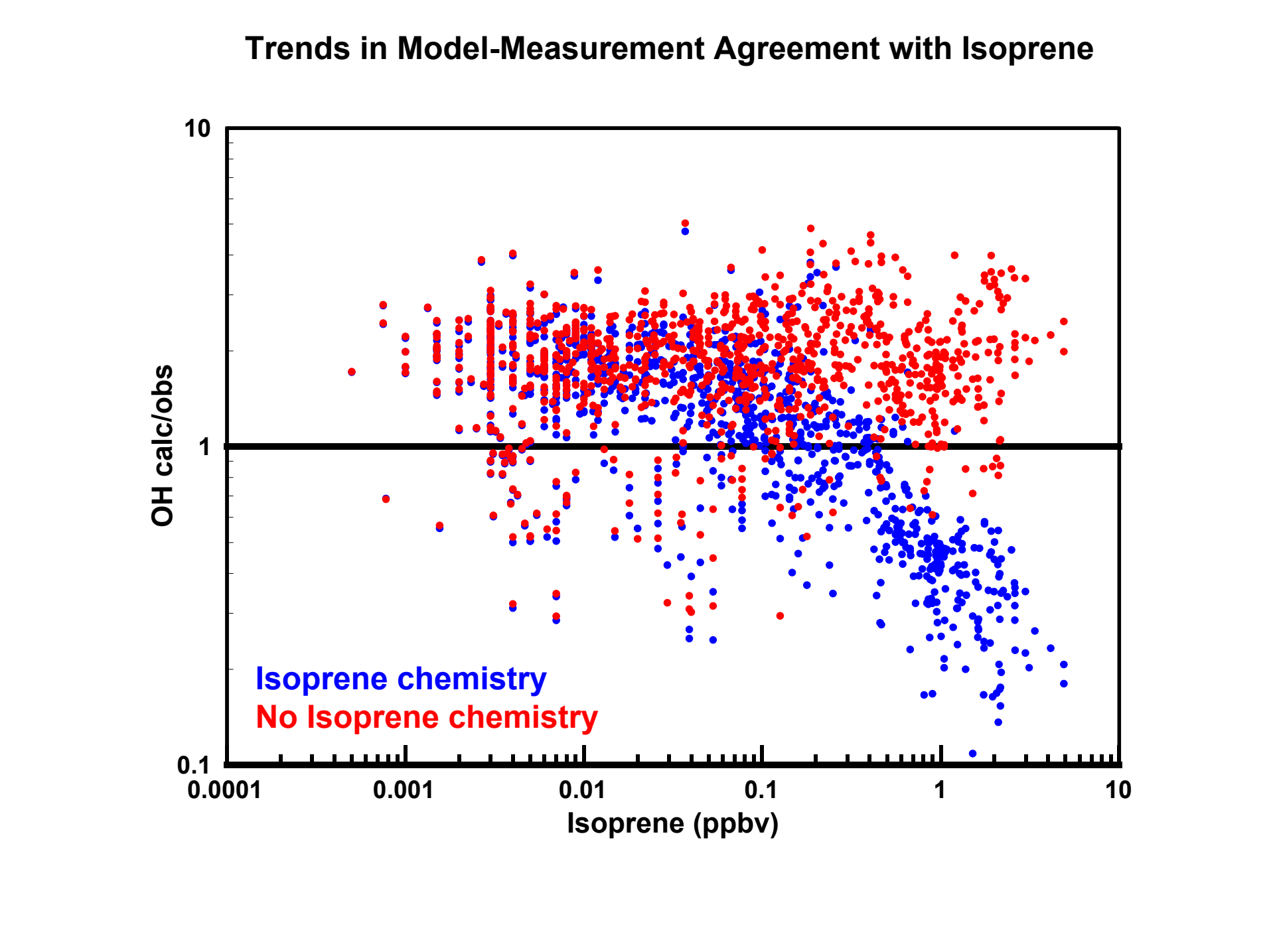

Trends in Model-Measurement Agreement with NO
HO2 and H2O2 calc/obs
10
1
0.1
0.01
0.001
0.0001
1
10
100
1000
10000
NO calc (pptv)
HO2
H2O2

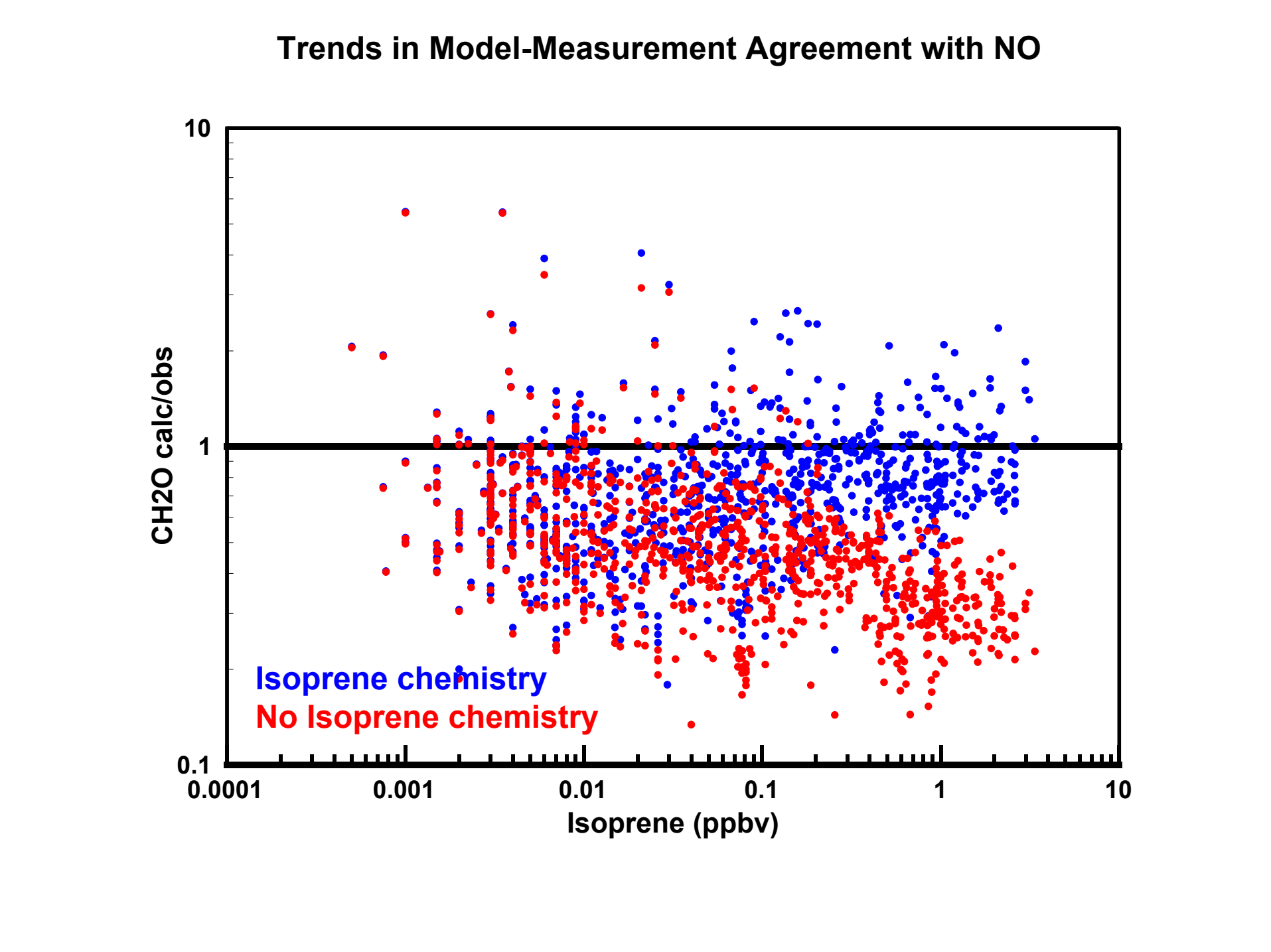

Trends in Model-Measurement Agreement with NO
HO2 and sqrt(H2O2) calc/obs
10
1
0.1
0.01
0.001
0.0001
1
10
100
1000
10000
NO calc (pptv)
HO2
sqrt(H2O2)


Trends in Model-Measurement Agreement with NO
HO2 and sqrt(H2O2) and HO2NO2 calc/obs
10
1
0.1
0.01
0.001
0.0001
1
10
100
1000
10000
NO calc (pptv)
HO2
sqrt(H2O2)
HO2NO2

Trends in Model-Measurement Agreement with Isoprene




Trends in Model-Measurement Agreement with Isoprene
10
1
0.1
OH calc/obs
0.0001
0.001
0.01
0.1
1
10
Isoprene (ppbv)
Isoprene chemistry
No Isoprene chemistry


Trends in Model-Measurement Agreement with NO
10
1
0.1
CH2O calc/obs
Isoprene chemistry
No Isoprene chemistry
0.0001
0.001
0.01
0.1
1
10
Isoprene (ppbv)

Summary

INTEX offers an unprecedented number of measurements suitable for testing photochemical theory.

Comparisons are somewhat paradoxical

Current estimated ozone production rates for the upper troposphere are 4-5 ppbv/day (could it be closer to 10 ppbv/day!?)

Input from the Science Team regarding these and other applications of the model are welcomed.